

NATURAL WATER ANALYSIS BASED ON MULTISENSOR SYSTEM

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Abstract: Novel back-side contacts structures of ISFETs (ion-selective field effect transistors) are described in this paper. Back-side contact type transducers, constructed in the Institute of Electron Technology, (Warsaw, Poland) are especially suitable for the design of chemical sensors for multiparameter flow analysis. The sensor structure requires a specialized flow-head, allowing the measurement of the signals of 10 ISFETs. The flow head was designed and manufactured in a form of 10-arm round module. A fully computerized flow set-up governed by special software developed under LabView environment was used in the measurements. Unmodified transducers with Si_3N_4 gate are H^+ -sensitive and can be used as solid-state pH sensors. After the preliminary tests the ISFETs were covered with ion-selective membranes to construct sensors for the determination of chosen ions. The calibration process of Na^+ , Ca^{2+} , NO_3^- - sensitive CHEMFETs, their performances (selectivity coefficients, slopes, response times) and the results of determination of the ions in lake and Oligocene water are presented.

INTRODUCTION

Chemical sensors are finding more and more applications in chemical analysis, environmental monitoring, medicine, industry etc. A great number of chemical sensors have been developed and commercialized over the last decades [1,2]. The fast growing market and requirements such as low price and small sample consumption are the driving force for the design of miniaturized sensors e.g. based on field effect transistor. The ISFET (ion-selective field effect transistor), as a solid-state sensor based on silicon technology, can be an attractive alternative to the classical potentiometric sensor, exhibiting comparable analytical performances. It can be constructed as a front-side contact structure (applied as a batch type sensor when mounted on the epoxy support with encapsulation) or back-side contact structure (suitable for flow analysis). The design of back-side contact ISFETs eliminates the necessity of the structure encapsulation. However, back-side type structures should be mounted in specialized cells, allowing their introducing in the measured medium. The most attractive is the construction of the sensor flow-through cell, which enables the measurement of the signals of ISFETs being in contact with the flowing solution. Up to now a few flow devices were described in the literature [3-6]. Most of published flow-cells were strictly dedicated to one type of the sensors e.g. (ISFETs, solid state electrodes, amperometric sensors) which limited their applications in sensors population evaluation or multiparameter monitoring.

Monitoring of water composition is an important field of research and seems to be much more interesting when several components can be measured simultaneously. Nowadays ground waters have only been controlled in time- and space-limited intervals and the various sampling have been accompanied by expensive analysis. This procedure gave no information

about possible fluctuations of concentrations of the measured components occurring in the meantime. This problem can be solved by the use of the flow system based on the versatile head with optional configurations of various chemical sensors

EXPERIMENTAL

Sensors structures. The designed back-side contact ISFETs with Si_3N_4 gate were manufactured in the Institute of Electron Technology using a traditional IC microtechnology. The main idea of the FET design was to make it compatible with a flow-head developed and described in the previous work [7,8]. Thus a square 5 by 5 mm back-side types structures were prepared (see Fig.1).

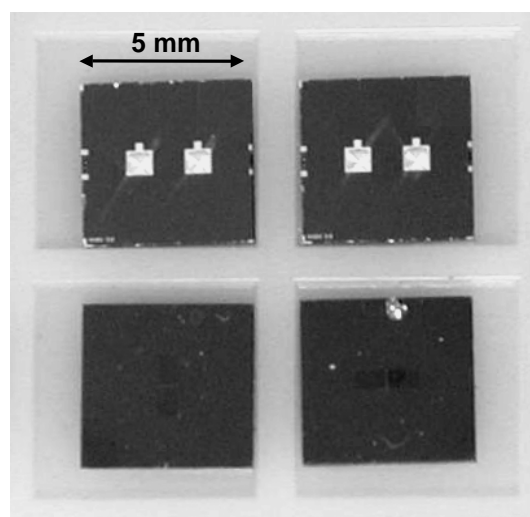


Figure 1. Back-side contact structures of ISFETs.

Apparatus. The flow set-up consists of: a designed flow-through head (cross section of the round head is given in Fig. 2), a peristaltic pump (Gilson Miniplus 3),

an automatic burette (Metrohm Dosimat), a sensor amplifier, a 12-bit data acquisition PC-card (PCI 6025), and a personal computer for system management. Miniaturized chemical sensors are mounted in implants placed on the rim of the cell body (see Photograph 1). Special application software created in LabView (National Instruments) was used in the measurements.

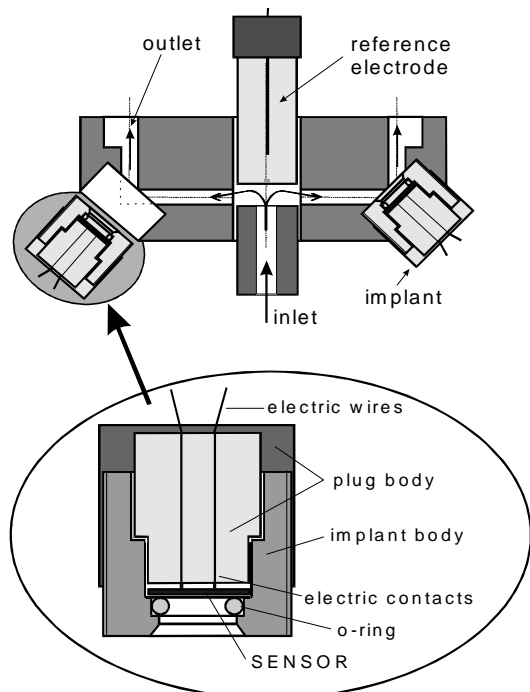
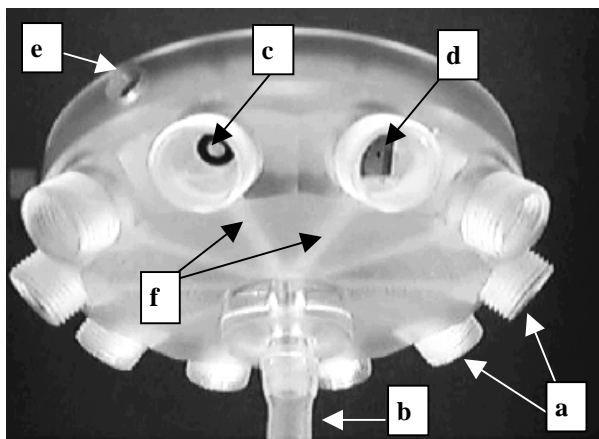


Figure 2. Cross section of the flow head.



Photograph 1. 10-sensor flow head: a. implants, b. inlet tubing, c. mounted o-ring, d. mounted back side contact ISFET, e. outlet, f. flow channels.

Chemicals. All salts used were of analytical grade and were purchased from Fluka. The standard stock solutions (0.1 mol l^{-1}) of metal nitrates were prepared in redistilled water, working solutions were obtained by dilution of the stock solutions.

The ionophores (Na^+ - 4-tert butylcalix[4]arene-tetraacetic acid tetraethyl ester, Ca^{2+} - ETH 1001, NO_3^- - tetradodecyl ammonium nitrate), the lipophilic salt - potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (KTFPB), *o*- nitrophenyl octyl ether (*o*-NPOE), poly(vinyl chloride) (PVC), siloprene K1000 and curing

agent K11 were obtained from Fluka and used for sensing membrane preparation. Freshly distilled tetrahydrofuran (THF, from Fluka) was used as a solvent for the membrane components.

CHEMFETs' Preparation. Before the membrane deposition, the polyHEMA was conditioned over 3 hours in an aqueous solution of the internal electrolyte. The membrane solution (approximately $10 \mu\text{l}$) was deposited on the gate oxide surface of FET covered with poly(2-hydroxyethyl methacrylate) (polyHEMA) layer, which provides thermodynamically well-defined membrane-gate interface. After membrane solvent evaporation, the sensors were mounted in the flow-cell system and were conditioned during 24 hours before the use.

Measurements. The measuring conditions of FETs: constant drain-current mode $I_D = 0.1 \text{ mA}$ and source-drain potential $V_{DS} = 0.5 \text{ V}$. All measurements were carried out at room temperature.

The response time ($t_{95\%}$) of the sensors was evaluated by measuring the time required to achieve 95% of the stable potential after changing concentration of primary ion in solution of 0.1 M Mg^{2+} as an interfering ion. Potentiometric selectivity coefficients [$\log K_{ij}$] were found according to the fixed interference method (FIM) [9] increasing the activity of the primary ions in the solutions in steps of 0.5 pM^{n+} and 0.5 pX^{m-} . The titration was initiated after signals of the sensors were stabilized (about 15 min). After each concentration change, the data points were collected for 10 min. The activities of ions in aqueous solutions were calculated according to the Debye-Huckel approximation.

RESULTS

Preliminary tests of new ISFET structures.

Constructed back-side contact ISFETs with Si_3N_4 gate are H^+ -sensitive and can be applied as solid-state pH sensors. In order to evaluate working properties of the structures, their pH responses were determined. The ISFETs signals (potentials) were measured in the flow-cell measuring set-up changing the pH of the pumped solution. The pH of the solution was measured using a combined glass electrode connected to a laboratory pH-meter. The pH responses of ISFETs are presented in Fig.3.

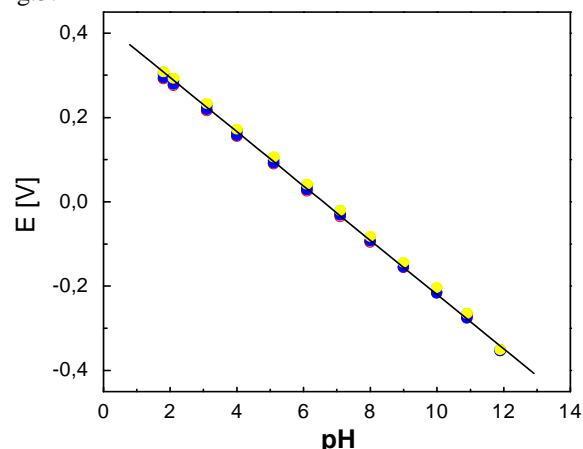


Figure 3. Relative changes of ISFET potentials versus pH.

Excellent linearity of the structures was observed with the average sensitivity about 58-60 mV/pH. The dependence of the sensor signals as a function of time was checked when three buffer solutions (pH=4.0, 7.0 and 9.0) were successively pumped into the flow-head. The response time of ISFETs does not exceed 10 s when the pH was changed from acidic to alkaline. However, it was observed that the response time increased to a few minutes when the pH of the solution was changed from alkaline to the acidic range. Constructed back-side contacts ISFETs exhibited good performances and enables the accurate determination of pH directly in the sample. Moreover, further deposition of an ion-selective polymer membrane on the ISFET surface allows obtaining a sensor for the determination of a chosen ion.

Multiion analysis. There were ten chemical sensors mounted in the head: three Na⁺-, three Ca²⁺- and four NO₃⁻ sensitive CHEMFETs. The potentiometric selectivity coefficients were determined and the average values of log K_{i/j} are shown in Table 1.

All sensors exhibited slopes of more than 50 mV per decade (for monovalent ions) and more than 28 mV per decade for Ca²⁺, response times less than 60 s. The detection limits of analysed ions were estimated as 1.58x10⁻⁵M; 3,98x10⁻⁶M; and 7.94x10⁻⁶M for Na⁺, Ca²⁺ and NO₃⁻ ions, respectively.

Calibration and recalibration of the sensors in the system by measuring full range calibration curves seems to be time consuming and quite difficult from technical point of view (number of containers with standard solutions, multi-port valves). To simplify the analytical procedure three calibration solutions containing all analysed ions and the carrier have been proposed.

During the measurements samples of water were delivered to the laboratory and measured in continuous-

Sonnenborn [17]) German drinking water from different purification plants contained 1-530 mg/dm³ of Na⁺ (average of 954 samples is 73 mg/dm³).

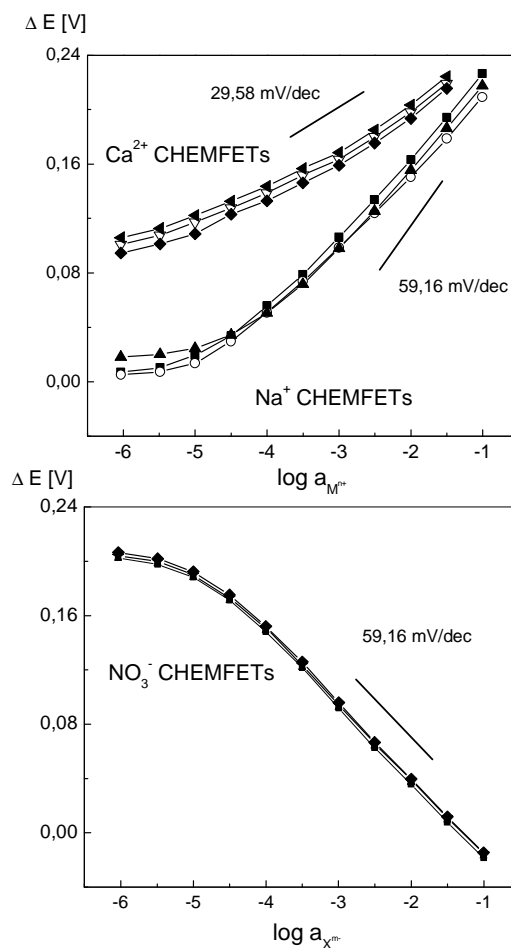


Figure 4. Full range calibration curves of sensors in carrier solution (0.005M CH₃COOLi)

Table 1. Selectivity coefficients (log K_{i/j}) of the sensors used for multi-ion analysis.

SENSOR	Interfering ion					
	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺
Na ⁺ - CHEMFETs	-2.2	-	-2.3	-1.8	-2.8	-3.6
Ca ²⁺ - CHEMFETs	-2.6	-3.6	-3.0	-3.1	-	-3.9
	CH ₃ COO ⁻	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Br ⁻	NO ₂ ⁻
NO ₃ ⁻ - CHEMFETs	-3.2	-3.7	-4.2	-2.9	-1.8	-1.5

flow system so this mode can be called *quasi*-monitoring. Solution of CH₃COOLi (0.005M) was chosen as a carrier. The concentrations of specific ions in the calibration solutions were chosen from the linear range of calibration curves performed in the carrier solution (see Fig. 4). The ionic strength of the calibration solutions was maintained on the same level. The linear ranges of the calibration plots of the sensors are in a concentration range relevant to monitor water from deep intakes, natural and waste waters [15]. In Polish largest river – Vistula for example fluctuations of concentrations of Na⁺, Ca²⁺, and NO₃⁻ ions were determined as 2.4-121.0 mg/dm³, 18.5-115.0 mg/dm³ and 0.05-5.4 mg/dm³ respectively [15]. In Great Britain drinking water intakes sodium content was determined between 2 and 90 mg/dm³ [16]. In 1980 (according to

The carrier, calibration solutions and samples of waters were pumped into the head from separate containers and responses of the sensors were collected and plotted in real time on the monitor of the computer governed the measurement system. Flow rate of the sample solution was not higher than 2.0 ml/min in each channel of the flow head. It was enough to make the head deaerated. In the preliminary measurements the calibration was repeated after every three samples determinations in order to avoid measurement errors caused by the sensors signal drift. However, quite stable signals of all used sensors both during calibration solutions measurements and samples analysis confirm possibility of calibration not often than once for three hours. The equations of the calibration curves for analysing ions were estimated using the least squares linear regression method

attached as a data analysis procedure to the Microcal Origin 6.0 software. Results of Na^+ , Ca^{2+} and NO_3^- ions determinations in deep intakes water samples and the lake water are shown in Table 2.

Table 2. Ion concentrations in water samples (mg/dm^3) compared with the results obtained using reference analytical methods.

Ion	Intake 1 Warsaw, Rommera St.	Intake 2 Warsaw, Ciszewskiego St.	Lake water Żyrardów, St. John's Pond
Na^+	17.5 ± 0.7 *	176.8 ± 10.5	757.5 ± 12.1
	18.4 ^a	174.3 ^a	752.0 ^a
Ca^{2+}	119.5 ± 3.1	48.7 ± 3.9	104.5 ± 4.1
	120.0 ^a	49.1 ^a	104.4 ^a
NO_3^-	- **	4.4 ± 0.2	117.0 ± 2.9
	0.2 ^b	4.4 ^b	118.1 ^a

*- the uncertainty values were estimated using t-Student test for $\alpha = 95\%$, $n = 9$ and $t_{\alpha, n-1} = 2.3060$

** - below the detection limit of NO_3^-

^a - atomic absorption spectrometry,

^b - UV-Vis spectrophotometry,

They are in good agreement with those obtained using different, reference analytical methods. In water samples with ionic strength values less than 0.1 not more than 5% of total sodium and 10% of total calcium content can occur in a complex form [15]. Despite of high ionic strength of the lake water sample, the results of Na^+ and Ca^{2+} ions determination were also comparable with those obtained using reference analytical methods. It could indicate the absence of strong complexing compounds both in oligocene and lake water samples.

Short response times (approx. 60 s) for all used sensors were observed not only during preliminary tests of the sensors but also when real samples were analysed. However, time which is needed to the Na^+ - and NO_3^- - CHEMFETs achieved stable potential after sample determination (the reverse time) should be improved. The reverse time is not so important if waters from large reservoirs monitored because fluctuations of ion concentrations that can occur have not so dynamic character. In case of using proposed flow system for on-line analysis of various water streams it becomes very important. The sudden fluctuations of ions concentrations can be miscalculated or missed at all. There is also possibility of using the proposed system in FIA measurements but then the sensors with long reverse time can limit the number of analysed samples in the time unit.

Conclusions

Results of the real samples measurements show that multi-ion water analysis using versatile flow head with mounted sensors is a suitable analytical method for this

purpose. The proposed technique is more comfortable than time-consuming classical analytical procedures with complicated samples pre-treatment. Moreover, the head flexibility gives great prospects of automation of analytical process and using ISFETs, solid state electrodes and optrodes in optional configurations for the construction of a portable analyzers. These systems can be wastewater and natural water resources. Due to their small size, the developed sensors can also be used in miniaturized flow-cell and flow injection analysis systems as well as detectors in miniaturized analytical systems - μTAS . The IC technology allows mass production of the sensors. Moreover, the technology of UV-polymerizable ion-sensitive membrane deposition is compatible with the IC technology and enables the production of cheap chemical sensors.

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